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Investigation and characterization of polypropylene plastic waste pyrolysis oil: Effect of temperature and fractional condensation

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ABSTRACT

The escalating accumulation of polypropylene (PP) plastic waste poses significant environmental challenges, requiring innovative waste management strategies. Pyrolysis of plastic waste presents a promising approach for sustainable production of alternative fuels. However, pyrolysis oil possesses undesirable properties for direct fuel applications, requiring additional upgrading steps before being utilized for specific purposes. Fractionation offers an effective method for the separation of pyrolysis oil. This study investigates the pyrolysis of PP plastic waste with three-stage condensers system, focusing on the effect of temperature and fractional condensation on the yield and characteristics of pyrolysis oil. Experiments were conducted within temperature range of 400, 410, 425, 430, 440, to 450 °C, with the aim of optimizing the generation of liquid products. The pyrolysis vapors were sequentially passed through three condensers. Results indicate that the maximum bio-oil was obtained at 450 °C as optimum temperature, which consists of 2.32% gases (C_1-C_5) , 41.94% gasoline (C_6-C_{11}) , 44.15% kerosene $(C_{12}-C_{20})$, and 11.59% residue (> C₂₀). The distribution of compounds was influenced by fractional condensers, with the highest relative contents of compounds obtained from condenser 1, 2, and 3 were gasoline (79.28%), kerosene (51.97%), and gasoline (55.21%), respectively. Gas Chromatography-Mass Spectrometry (GC-MS) was used to characterize the chemical and physical properties of bio-oils. The characterization results reveal that the pyrolysis oil obtained from PP plastic waste are dominated with 1-heptene-5-methyl (C₈H₁₆). The composition of pyrolysis oil demonstrated favourable and suitable properties for potential applications as renewable fuels and chemical feedstocks.

Keywords: alternative fuel; pyrolysis; plastic waste; polypropylene; renewable energy.

INTRODUCTION

Bawean Island in Indonesia, like many other island communities, faces significant environmental challenges due to the plastic waste. The

island, located in the Java Sea, is affected not only by locally produced waste but also by marine debris that is carried to its shores by ocean currents. Plastic waste has emerged as a significant environmental challenge due to its persistent

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nature and increasing production, with polypropylene (PP) is being one of the most commonly used thermoplastics worlwide. According to the Plastics Europe Market Research Group, PP accounted for approximately 30% of the total plastic production in 2020, highlighting its prevalence in various applications ranging from packaging to automotive components (Kumar et al., 2021)inadequate recycling, and deposits in landfills. In 2019, the global production of plastic was at 370 million tons, with only 9% of it being recycled, 12% being incinerated, and the remaining left in the environment or landfills. The leakage of plastic wastes into terrestrial and aquatic ecosystems is occurring at an unprecedented rate. The management of plastic waste is a challenging problem for researchers, policymakers, citizens, and other stakeholders. Therefore, here, we summarize the current understanding and concerns of plastics pollution (microplastics or nanoplastics. Although recycling attempts have been made, they remain largely ineffective, with only about 4% of materials recycled, leaving the bulk accumulation in landfills (Nayanathara Thathsarani Pilapitiya and Ratnayake, 2024). Figure 1 shows the composition of plastic waste collected in Bawean Island, which shows that PP and LDPE dominated the type of plastic waste. The improper disposal and accumulation of PP waste pose severe environmental threats, including soil and water pollution, and contribute to the growing global plastic crisis. Plastic wastes generates both direct and indirect costs to the global economy. Direct costs are linked to plastic pollution, degradation of marine

and terrestrial ecosystem, and government expenditures for cleanup efforts, while indirect costs include public health concerns (Sharuddin et al., 2016; Chang, 2023). Therefore, finding effective and sustainable methods to manage and recycle this waste is essential for reducing its negative environmental impacts.

Pyrolysis has risen as a promising solution for managing plastic waste. This thermal decomposition process occurs in an oxygen-free environment at temperatures between 300 and 800 °C, facilitating the transformation of plastic waste into hydrocarbons, which can subsequently be refined into fuels or chemical feedstocks (Hasan et al., 2023). Pyrolysis breaks long hydrocarbon chains into shorter ones, which upon cooling, condense into a liquid fuel (oil). To produce 1 kg of plastic, approximately 1.75 kg of petroleum is required to meet both the raw material and energy demands of of the process (Kumar et al., 2011). Different types of plastics, including polypropylene (PP), polyethylene (PE), and polystyrene (PS) have calorific values comparable to petroleum-derived fuels like gasoline, diesel, and kerosene (Faisal et al., 2023; Khazaal and Abdulaaima, 2023). Thus, converting plastic waste into fuel through thermal decomposition can be a promising option for recycling plastic that cannot be mechanically recycled due to economic consideration.

The properties of the pyrolysis oil generated are heavily influenced by the type of plastic waste used, the pyrolysis temperature, and the heating rate applied throughout the process (Gonzalez-Aguilar et al., 2022). The yield and quality of

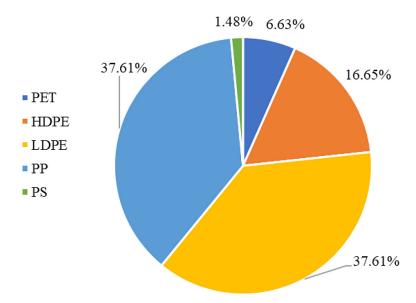


Figure 1. Composition of plastic waste by the type in Bawean Island, Indonesia

pyrolysis oil are significantly influenced by various factors, including the pyrolysis temperature, type of plastic, and the presence of catalysts (Dai et al., 2024). The temperature plays a crucial role in determining the composition and quality of pyrolysis oil. Research indicates that higher temperatures tend to favor the production of liquid products while reducing the solid residue. Specifically, temperatures ranging from 350 to 600 °C C are commonly studied to optimize the composition of pyrolysis oil derived from PP. The chemical composition, energy content, and physical properties of the resulting pyrolysis oil are essential for assessing its potential as a renewable energy source (Riesco-Avila et al., 2022; Thahir et al., 2021)19, and 28 °C/min were evaluated through an experimental multi-level design. The results show that higher temperatures or lower residence time reduce the yield of pyrolytic oil at the expense of increasing the yield of gaseous products. The maximum liquid yield was 69%, obtained at 410 °C and a heating rate of 10 °C/min. The composition of pyrolytic oil covers a wide range of hydrocarbons; thus, a fractionation is necessary before using it as fuel in internal combustion engines. The fractionation process yielded 21.12 wt% of light fraction (gasoline-like.

Pyrolysis oil is a complex blend of oxygenated hydrocarbons and is not suitable for direct use as an alternative fuel. It often possesses several unfavorable characteristics for fuel applications, such as high water content and corrosiveness, increased acidity, and low thermal stability (Mati et al., 2022; Tumbalam Gooty et al., 2014). Recently, fractional condensation of hot pyrolysis vapors has emerged as a promising approach for separating the constituents of pyrolysis oil. This method offers main advantage in reducing thermal energy demand compared to other techniques, such as vacuum and flash distillation, which face technical challenges during the separation process (Kim, 2015). In pyrolysis, condensers play a critical role to transforming polymeric materials into liquid fuels, gases, and char. As the pyrolysis vapors exit the reactor at high temperatures, the condensers cool the gases, causing the condensable vapors to liquify. This gas-to-liquid transition is crucial for the collection of oils, which are main end-products of the pyrolysis process. The fractional condensation process involves directing the vapor stream of pyrolysis oil through a sequence of condensers, each set at progressively lower temperatures. This method facilitates the

separation and collection of liquid fractions, each exhibiting specific chemical components within the respective condensers (Chai et al., 2020; Wang et al., 2019).

Additionally, pyrolysis oil separation methods have to demonstrate economic and environmental feasibility. Since distillation of pyrolysis oil has its limitations, this study explores fractional condensation as an effective alternative to enhance the quality of pyrolysis oil and concentrate specific chemical components. The objective of this research is to examine how temperature influences the pyrolysis of PP plastic waste using fractional condensers, focusing on the characterization of the bio-oils. The analysis of the yield and composition of bio-oil fractions were utilized to evaluate the process of fractionation. Understanding the relationship between temperature, fractional condensation, and bio-oil properties will provide insights into optimizing the pyrolysis process for enhanced energy recovery and waste management. This research findings could contribute to the development of sustainable practices for managing plastic waste and promotes the circular economy.

MATERIALS AND METHODS

Materials and sample preparation

PP plastic waste was selected as feedstock for this research. PP plastic waste was sorted and collected from one of municipal waste collecting points in Bawean Island, Indonesia. Before conducting the experiment and analyses, the PP plastic waste samples underwent a series of pretreatment, including washing, drying, and shredding to reduce the sample particle size.

Pyrolysis process

Experiments were performed in the pyrolysis reactor made of stainless steel with three-stage condensation configurations as presented in Figure 2.

To optimize the pyrolysis reaction temperature, experimental runs were conducted at reactor temperatures of 400, 410, 425, 430, 440, and 450 °C. All the experimental runs were conducted for 75 minutes for the pyrolysis of 1 kg PP plastic waste samples. After pyrolysis, the vapor produced in the reactor first passes through Cyclone for initial separation of biochar. Subsequently, the pyrolysis vapor is cooled

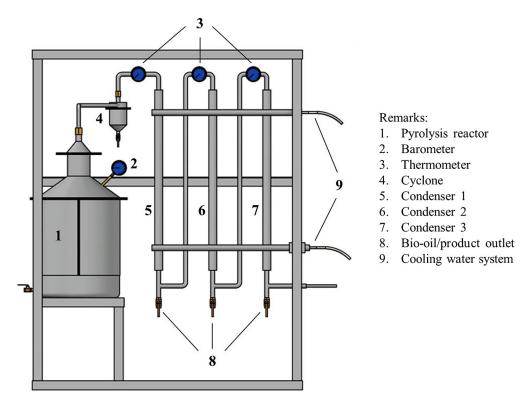


Figure 2. Schematic diagram of reactor system for PP plastic waste pyrolysis

and condensed into bio-oil using three sequentially arranged fractional condensers (Condenser 1, Condenser 2, and Condenser 3) with cooling water. The cooling water flows in the reverse direction, from Condenser 3 to Condenser 1. After condensation, the produced bio-oils were collected separately in each product outlet for Condenser 1, Condenser 2, and Condenser 3. The gases that do not condense from the system are vented away. To determine the total yield of bio-oil, the products collected from the cyclone and the three condensers were weighed. Each fraction of bio-oil recovered from the condensers was analyzed separately.

Characterisation of raw materials

Before being used as pyrolysis feedstock, dried samples of PP plastic waste were subjected to thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) experiments using Pyris Diamond TG/DTA Instrument from Perkin Elmer Co. (USA). The experiment was conducted over a temperature range of 30–800 °C at a heating rate of 10 °C/min. Result from this analysis helps to determine the temperatures at which the sample decompose and optimize the pyrolysis temperature settings.

Characterisation of bio-oil products

The chemical compounds in the bio-oils collected from the cyclone and all three condensers (Condenser 1, Condenser 2, and Condenser 3) were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The analysis was performed using Shimadzu AOC-20i Instrument (Japan). Before being injected into the instrument, suspended particles in the oil were removed using a 0.45 µm filter.

RESULTS AND DISCUSSIONS

TGA-DTG results of PP plastic waste

The thermal decomposition of PP was carried out to provide detailed information on the thermal stability and composition of the sample. The TGA and DTG curves for the PP plastic samples is shown in Figure 3. It is noted that the primary decomposition of PP occurred within the range of 300–500 °C. This result aligns with previous studies indicating that the mass loss of PP begins around 350 °C and is nearly complete at around 480 °C (Jung et al., 2010; Majewsky et al., 2016; Mortezaeikia et al., 2021). The temperature at

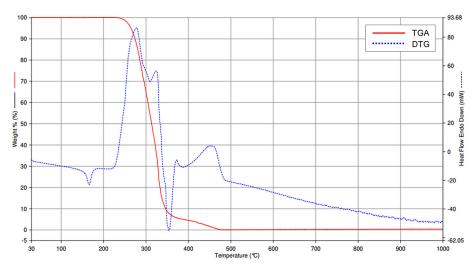


Figure 3. TGA and DTG curves of the PP plastic waste samples

which 50% of the mass is decomposed is approximately 450 °C (Hassibi et al., 2023).

Bio-oil distribution in different temperatures and condensers. Temperature is an important factor in determining both the yield and quality of pyrolysis oil. In this study, temperatures ranging from 400 to 450 °C were used. Table 1 presents the volume distribution of bio-oil generated from the pyrolysis of PP plastic waste at various temperatures. Results indicate that the pyrolysis temperature significantly influences the quantity of bio-oil produced and the efficiency of condensation process. At the pyrolysis temperature of 400 °C and 410 °C, the production of biooil is only observed in Cyclone and Condenser 1. As the temperature increases to 430 °C and 440 °C, the bio-oil captured in Condenser 2 and Condenser 3 increased, indicating its effectiveness in condensing heavier fractions that escape from Cyclone. At temperature 450 °C, a significantly large amount of bio-oil was obtained from Cyclone and all condensers and indicated as the highest volume.

The bio-oil distribution across the three stages of condensation of the bio-oil recovery system is illustrated in Figure 4. It is shown that the fractional condensations and temperatures significantly affect the quantity of bio-oil produced. At higher temperature, the distribution of bio-oil yield is more evenly spread across the condensers. This result suggests that higher temperatures facilitate the release of more hydrocarbons, which are then effectively condensed. The pyrolysis reaction is more likely to reach completion at higher temperatures. Higher pyrolysis temperatures lead to an increase yield of liquid products due to several thermochemical mechanisms occur during the decomposition of materials (Sui et al., 2014). Moreover, at higher temperatures, the energy provided allows for greater fragmentation of the PP constituents into smaller molecules increased. Thus, the process of devolatilization, which is the release of volatile compounds, is also enhanced at higher temperatures. This is attributed to the breakdown of larger organic molecules and long-chain polymers into smaller and more volatile fragments, subsequently condensed

Table 1. Volume of bio-oils collected in the cyclone and each condenser at different pyrolysis temperatures

Temperature process (°C)	Bio-oil volume (ml)				
	Cyclone	Condenser 1	Condenser 2	Condenser 3	Total
400	420	199	0	0	619
410	525	378	0	0	903
425	756	182	69	0	1007
430	400	395	200	10	1005
440	310	370	140	137	957
450	301	390	290	153	1134

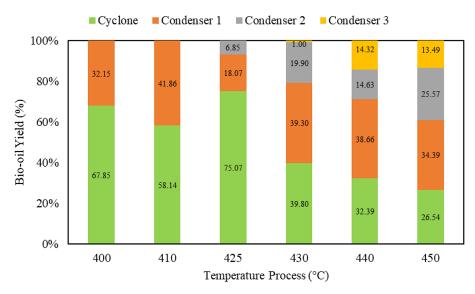


Figure 4. Yield of bio-oils collected in the cyclone and each condenser at different pyrolysis temperatures

to form bio-oil (Aboelela et al., 2023; Mohamed et al., 2014) which may be broken down into combustion, torrefaction, pyrolysis, hydrothermal liquefaction, and gasification. In this study, producing biofuels using a biomass pyrolysis process was investigated. This study explored the pyrolysis process and operating conditions to optimize the process parameters to maximize the desired product yields and quality. The pyrolysis process produces three main products, which are bio-oil, bio-char, and gas. There are three classifications for the pyrolysis method, with each of them producing a majority of a certain product. First, slow pyrolysis is conducted in the temperature range of 300-950 °C and residence time of 330-550 s. It produces around a 30% oil yield and 35% char yield, and thus, the majority yield of slow pyrolysis is char. Second, fast pyrolysis produces around 50% oil, 20% char, and 30% gas yields with a temperature range of 850-1250 °C and a residence time of 0.5-10 s. The average yield of flash pyrolysis was found to be 75% bio-oil, 12% bio-char, and 15% gas, which is conducted within less than 1 s. It was reported that the pyrolysis of biomass was simulated using ASPEN Plus, where the effects of several parameters, such as the temperature, heating rate, and residence time, on the product yield and composition were investigated. Pyrolysis was performed under different conditions ranging from 400 to 600 °C. The effects of different catalysts on the pyrolysis process were studied. It was found that the addition of a catalyst could increase the yield of bio-oil and improve the quality of the product. The optimal

operating condition for the pyrolysis process was determined to be a temperature of 500 °C, which resulted in a higher bio-oil yield. It was found that the biofuel yield was enhanced by selecting appropriate raw materials, such as rice husk, along with the pyrolysis temperature (e.g., 450 °C).

Using fractional condensers in pyrolysis process led to higher yield of bio-oils due to enhanced separation and recovery capabilities at different thermal stages of condensation. This effectiveness can be attributed to the ability of multiple condensers to capture a wider range of vapors produced at various temperatures during pyrolysis. In this study, a configuration of threestage condensation was utilized. Condenser 1 captures the heaviest and highest boiling point compounds, while Condenser 2 and Condenser 3 are set at lower temperatures to condense lighter and lower boiling point compounds. In this study, a temperature of 450 °C was selected as the optimum condition for the pyrolysis of PP plastic waste to achieve the maximum yield of bio-oil. This temperature ensures that vapors from pyrolysis process are condensed effectively by using three condensers.

GC-MS analysis of pyrolysis oil

One of the analytical techniques used to characterize pyrolysis oil is GC-MS. The oils collected from each condenser at different temperatures were analyzed using GC-MS to identify the chemical compounds present. The GC-MS result indicated that the obtained oils contain a

wide range of valuable chemical compounds. The chemical compounds detected were then organized into 4 typical hydrocarbons: gases (with carbon chain-length within the scope of C_1-C_5), gasoline (carbon chain-length of C_6-C_{11}), kerosene (carbon chain-length of $C_{12}-C_{20}$), and residue (carbon chain-length higher than C_{20}) (Habyarimana et al., 2017; Wang et al., 2015). The relative percentages of each fraction chemical compounds in the obtained bio-oils at different pyrolysis temperatures as detected by GC-MS is illustrated in Figure 5 and 6.

Figure 4 and 5 shows the effect of temperatures on the yield of hydrocarbon fractions (gases, gasoline, kerosene, residue) during pyrolysis of PP plastic waste. This result could be subjected for optimizing pyrolysis process of PP plastic waste based on temperatures. For instance, if the objective is to maximize kerosene

yield, operating at around 425 °C would be more suitable. Conversely, for higher yields of gasoline, temperatures around 450 °C is suggested. Results from GC-MS spectra also show that PP plastic waste during pyrolysis tends to mixed, demonstrating the potential for producing multiple fuel types from a single feedstock. The dominant fractions of bio-oil were compounds with carbon atom number C_6 – C_{11} and C_{12} – C_{20} . This result is supported with findings from previous studies which reported that pyrolysis oil from plastic waste contained a mixture of gasoline, kerosene, and diesel fractions, indicating the potential of substitution fuel (Desnia et al., 2024; Kumar and Singh, 2011).

To investigate the effect of fractionation condensation, the profile of each condenser on the composition of bio-oil obtained from pyrolysis process is studied. During fractional

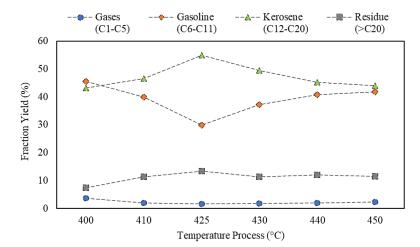


Figure 5. Effect of pyrolysis temperatures on the yield of chemical compounds present in bio-oils

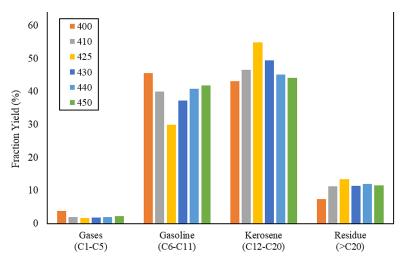


Figure 6. Distribution of major fractions present in bio-oils obtained from pyrolysis of PP plastic waste at different temperatures

condensation, a series of condensers operating at progressively lower temperatures is employed to capture different fractions of chemical compounds. As illustrated in Figure 7, the selection of bio-oil products collected from the cyclone and all condensers at different pyrolysis temperatures reveals that the major compounds of PP plastic waste pyrolysis are gasoline and kerosene. The yield of gasoline decreased while the yield of kerosene increased when the condensed temperature descended. Moreover, the concentration of

heavier compounds in the bio-oil increases with a reduction in condensing temperature (Raymundo et al., 2022; Westerhof et al., 2011). It is important to note that while fractional condensers influence the distribution of fractions, the configuration is more effective at pyrolysis temperatures exceeding 430 °C. The GC-MS spectrum of bio-oils obtained from Condenser 3 at the optimum temperature of 450 °C is presented in Figure 8. Based on GC-MS result, it appeared that 1-heptene-5-methyl (C_8H_{16}) was the major species present in

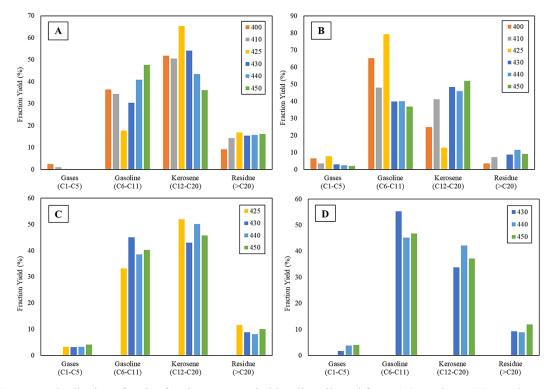


Figure 7. Distribution of major fractions present in bio-oils collected from: (A) Cyclone, (B) Condenser 1, (C) Condenser 2, and (D) Condenser 3 during pyrolysis of PP at temperature 450 °C

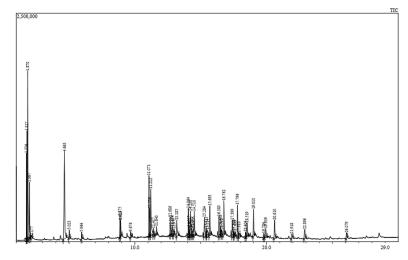


Figure 8. GC-MS spectra of oils obtained from pyrolysis of PP plastic waste at temperature 450 °C

the bio-oil obtained at optimum temperature when three condensers were used. 1-heptene-5-methyl is a hydrocarbon belonging to the category of alkenes. This compound is also recognised as one of primary components of gasoline fuel.

CONCLUSIONS

This study focused on examining how temperature and fractional condensation affect the pyrolysis process of PP plastic waste, highlighting the role of temperature control in optimizing the conversion of PP plastic waste into valuable products. The application of fractional condensers influenced both the yield and physicochemical characteristics of the bio-oil produced. The characterization of bio-oil by GC-MS confirmed the importance of fractional condensations to control pyrolysis products composition. The maximum bio-oil obtained at optimum temperature (450 °C) were consists of 2.32% gases (C_1-C_5) , 41.94% gasoline (C_6-C_{11}) , 44.15% kerosene $(C_{12}-C_{20})$, and 11.59% residue (> C₂₀). It was found from characterization result that 1-heptene-5-methyl (C_oH₁₆) compound dominated the obtained biooil. The characteristic of PP plastic waste derived oils is similar to gasoline. The configuration of three-stage fractional condensation employed in this research not only maximizes the yield of chemical products constituents but also improves the overall efficiency and environmental sustainability of the process.

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